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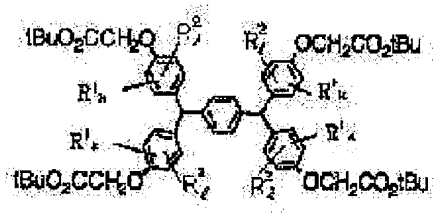
(54) 1,4-BIS(BIS(4-T-BUTOXYCARBONYLMETHYLOXYPHENYL)METHYL) BENZENE AND ITS DERIVATIVE



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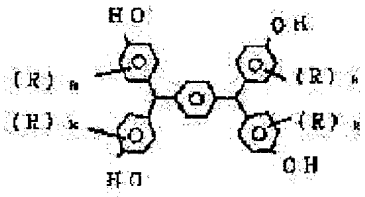

II

(57)Abstract:

PURPOSE: To obtain the subject compound having a specific mother nucleus structure and t-butoxycarbonylmethyl ether side chains, having high compatibility with polymeric compounds, and useful as a dissolution inhibitor for positive resists.

CONSTITUTION: The compound of formula I (R1, R2 are alkyl; (k) is 0-4; (l) is 0-2; wherein (k)+(l) ≤4). The compound is preferably obtained e.g. by dissolving 1,4-bis[bis(4-hydroxyphenyl)methylbenzene of formula II in DMF and subsequently reacting the compound of formula II with t-butyl chloroacetate in the presence of potassium carbonate at 60-100° C for 4-8hr.

LEGAL STATUS

[Date of request for examination]

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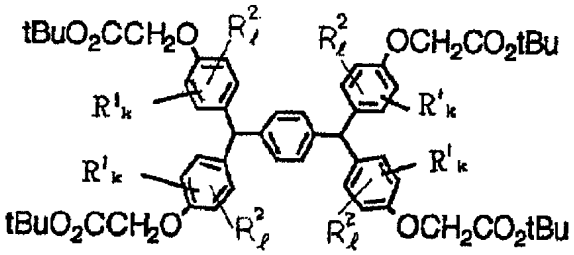
CLAIMS

[Claim(s)]

[Claim 1] 1 expressed with the following-ization 1, 4-bis[bis(4-t-butoxy cull BONIRUMECHIROKISHI phenyl) methyl] benzene, and its derivative;

[Formula 1]



However, R1 in ** 1 And R2 In an alkyl group and k, 0-4l (El) express the integer of 0-2. k+l<=4 [however,] -- it is -- every -- R1 and every -- R2 You may differ, even if the same.

[Claim 2] The same or the 1 and 4-bis[bis(4-t-butoxy cull BONIRUMECHIROKISHI phenyl) methyl] benzene indicated by claim 1 which a different alkyl group counts from the carbon atom which ether oxygen combines, and by which it is permuted by the 2nd place and the 6th place, and its derivative.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the effective new molecular entity as a lysis inhibition agent especially used for positives resist about a new compound.

[0002]

[Description of the Prior Art] Generally performing micro processing, such as a semi-conductor, conventionally using a resist is performed. In this case, in order that resolution may go up so that the radiation of short wavelength, such as high energy ultraviolet rays, an electron ray, and an X-ray, is used and wavelength becomes short, in order to acquire the process tolerance of 0.3 micrometers or less, developing a suitable resist to the radiation of short wavelength more is called for.

[0003] these radiations are used and the so-called chemistry magnification mold resist proposes as one approach for obtaining the resist of high sensitivity and high resolution -- having -- [H.Ito et al., Polym.Eng.Sci., 23 volumes, and 1023 pages (1983)] -- it has been observed. Especially this chemistry magnification mold resist in a positive type ** The two-component system resist which makes an indispensable constituent the high molecular compound which decomposes with an acid and becomes alkali fusibility although it does not dissolve in the compound which absorbs a radiation and generates an acid, and an alkali water solution (JP,2-209977,A etc.), ** The high molecular compound which decomposes with the compound, alkali fusibility high molecular compound, or acid which generates an acid with a radiation, and serves as alkali fusibility, And it is divided roughly into 3 component system resists (JP,2-245756,A etc.) which make an indispensable constituent the lysis inhibition agent which prevents the alkali dissolution of this high molecular compound, and decomposes with an acid, and loses this dissolution stopping power.

[0004] The imaging mechanism of 3 component system resist forms a positive image, when the very small acid which absorbs the irradiated radiation and is generated is made into a catalyst, a chemical reaction occurs in the both sides of a lysis inhibition agent or a lysis inhibition agent, and a high molecular compound and the solubility over the alkali developer of a high molecular compound increases only about the part where the radiation was irradiated by that cause.

[0005] Although very high practical sensibility was realized by the mechanism of such a chemistry magnification mold resist as compared with the conventional resist Since it is spread from [after an alkaline impurity advances from a resist front face and a substrate and irradiates a radiation] before development, an acid deactivates. The part which deactivated had the fault of producing the case where it becomes impossible to dissolve in an alkaline developer, and an exact image cannot be formed even if a radiation is irradiated.

[0006] It originates in this fault and the phenomenon in which a canopy top, such as T top, is formed in a pattern, or Susono called skirt length is made to a pattern near a substrate side is observed near the surface of a resist. For this reason, a chemical reaction occurs with the acid for which the radiation was irradiated and which was generated as engine performance required of a lysis inhibition agent, and not only the engine performance of enlarging the dissolution rate ratio of the part by which the radiation was irradiated, and the part which is not irradiated but when membranes are formed as a resist, the engine performance which makes late threshold speed to the inside of the film of an alkaline impurity is also required.

[0007] In order to fill the above-mentioned demand, it is desirable for a lysis inhibition agent to have high

compatibility to a high molecular compound, and to have comparatively higher lipophilicity. However, many of lysis inhibition agents [no] announced until now were what can fill these demands completely.

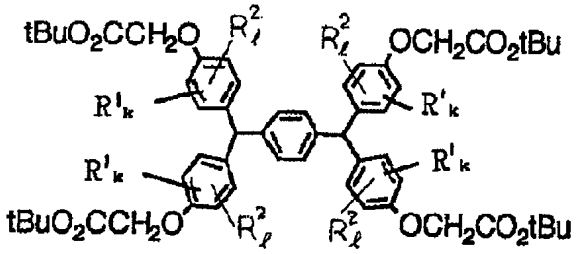
[0008]

[Problem(s) to be Solved by the Invention] Then, when this invention person etc. compounds various compounds, prepares a resist and the engine performance is examined, while finding out a series of mother-nucleus structures excellent in compatibility with a high molecular compound By using the t-butoxy carbonylmethyl ether as a side chain, it found out that contrast with high exposure part and non-irradiating part can be acquired, and that the resistance over penetration of an alkaline impurity could be given, and this invention was reached. Therefore, the purpose of this invention is to offer the effective new compound as a lysis inhibition agent for a positive resist especially.

[0009]

[Means for Solving the Problem] The above-mentioned purpose of this invention was attained by the 1 and 4-bis[bis(4-t-butoxy cull BONIRUMECHIROKISHI phenyl) methyl] benzene expressed with the following-ization 2, and its derivative.

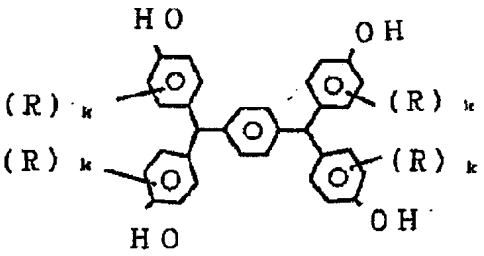
[Formula 2]



however -- R1 [however,] in ** 2 And R2 In an alkyl group and k, 0-4l (El) express the integer of 0-2. However, k+l is <=4. moreover, every -- R1 And R2 You may differ, even if the same.

[0010] The compound of this invention is easily compoundable by heating and stirring tert butyl chloroacetate and potassium carbonate moreover, after dissolving 1 expressed with the following-ization 3, 4-bis[bis(4-hydroxyphenyl) methyl] benzene, or its derivative in a suitable solvent.

[Formula 3]



[0011] R1 And R2 As an example, although a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, t-butyl, a pentyl radical, a neopentyl radical, a hexyl group, a cyclohexyl radical, etc. can be mentioned, for example, a methyl group, an ethyl group, an isopropyl group, etc. are desirable also especially in these. Moreover, as for especially k, it is desirable that it is 0, 1, or 2.

[0012] When using the compound of this invention as a dissolution inhibitor of 3 component positive resist so that it may mention later especially, it is R1 or R1 to 2 and the 6th place. And R2 Having permuted is desirable. As a solvent used at the time of composition, although DMF, DMSO, an acetone, etc. can be mentioned, it is desirable to use DMF also especially in these.

[0013] moreover, tert butyl chloroacetate -- or although it can change to it and bromoacetic acid-t-butyl, iodoacetic acid-t-butyl, etc. can also be used, it is desirable to use tert butyl chloroacetate from viewpoints, such as acquisition ease, handling nature, and reactivity. the same -- potassium carbonate -- or although it can change to potassium carbonate and a sodium carbonate, a lithium carbonate, etc. can also be used, it is desirable to use potassium carbonate or a sodium carbonate especially from viewpoints, such as reactivity.

[0014] Especially as long as the amount of these reactants used is more than the amount of theory that needs tert butyl chloroacetate, potassium carbonate, etc. to obtain the specified substance, it is not restricted, but since the above-mentioned reaction advances quantitatively, use of the amount of theory is sufficient. Although a reaction is performed stirring among 40 degrees C - 120 degrees C, it is desirable from compaction of reaction time, and a viewpoint of yield to make it react at 60 degrees C - 100 degrees C especially, and, as for the concentration of reaction mixture, it is desirable from viewpoints, such as economical efficiency, the solubility of a substrate, and reaction time, that it is 10 % of the weight - 50 % of the weight. If it is these reaction conditions, a reaction will be ended except for some exceptions in 4 hours - 8 hours.

[0015] It can perform easily carrying out separation **** of the specified substance from the reaction mixture after reaction termination by combining a well-known approach suitably. Since the compound of this invention is easily desorbed from a t-butoxy carbonylmethyl ether group and becomes alkali fusibility under existence of an acid while it has the mother-nucleus structure excellent in compatibility with a high molecular compound, it is especially effective as a lysis inhibition agent of the positive-resist ingredient of 3 component system.

[0016] The positive-resist ingredient of 3 component system is constituted by (A) lysis inhibition agent, the (B) acid generator, the (C) high molecular compound, and the (D) solvent like common knowledge. In this case, the weight ratio of A:B:C:D is 5-50:0.5-30:70-90:150-700, and is 10-25:2-8:75-85:250-500 preferably.

[0017]

[Effect of the Invention] Since the compound of this invention has high compatibility to a high molecular compound, it can be used in large quantities as a dissolution inhibitor into 3 component positive resist. Moreover, since lipophilicity is high, it has the effectiveness which an alkali impurity makes it hard to advance into the resist film from a resist front-face and substrate side.

[0018]

[Example] Hereafter, this invention is not limited by this although an example explains this invention to a detail further.

example 1.1 and 4-screw [bis(4-hydroxyphenyl) methyl] benzene 4.7g (0.01 mols) -- DMF50g -- dissolving -- 6.0g (0.04 mols) of tert butyls chloroacetate, and 5.5g (0.04 mols) of potassium carbonate -- in addition, 6-hour heating and stirring of were done at 80 degrees C.

[0019] After having added toluene 50g and 100g of water, having separated liquids, after cooling reaction mixture radiationally, and drying a toluene phase with magnesium sulfate, when reduced pressure distilling off

of the solvent was carried out, the oil-like reaction mixture was obtained. When the silica gel column chromatography (elution solvent: chloroform) refined this, 1 and 4-screw [bis(4-t-butoxy cull BONIRUMECHIROKISHI phenyl) methyl] benzene 6.3g (68% of yield) was obtained as a colorless crystal.

[0020] The decomposition point is 141 degrees C and is the following. It was checked from delta value of 1 H-NMR, and the result of elemental analysis that it is the above-mentioned compound.

1 H-NMR delta1.47 (s36H and t-bu-CH3), delta4.46 (s8H and -OCH2 CO), delta5.39 (s2H, Ph3 CH), delta6.79 (d 8H, Ph-H), and delta6.98 (d12H, Ph-H), elemental analysis (%)

Analysis value C:72.02, H:7.05, theoretical value C:72.24, H:7.14 [0021] 7.3g of colorless crystals whose melting point 1 and 4-screw [bis(4-hydroxy - 2, 6-dimethylphenyl) methyl] benzene 5.9g (0.01 mols) was used instead of example 2.1 and 4-screw [bis(4-hydroxyphenyl) methyl] benzene 4.7g, and also is 133-135 degrees C completely like an example 1 was obtained. Obtained crystal 1 H-NMR spectrum and the elemental analysis are as follows.

[0022] delta1.51 (s36H and t-bu-CH3), delta2.22 (s24H and Ph-CH3)

delta4.27 (s8H and -OCH2 CO), delta5.26 (s2H, Ph3 CH), delta6.70 (s8H, Ph-H), delta7.00 (s4H, Ph-H)

Elemental analysis (%)

analysis value C:73.49, H:7.88, and theoretical value C:73.68 and H:7.92 -- it was checked from this result and the result of ultimate analysis that the obtained compound is 1 and 4-bis[bis(4-t-butoxy cull BONIRUMECHIROKISHI -2, 6-dimethylphenyl) methyl] benzene. In addition, yield was 70%.

[0023] An example 3.1, a 4-screw [screw (4-hydroxy - [2 and 5-dimethylphenyl] benzene 5.9g (0.01 mols) was suspended in DMF50g, subsequently 6.0g (0.04 mols) of tert butyls chloroacetate and 5.5g (0.04 mols) of potassium carbonate were added, and 6 hour heating and stirring of were done at 100 degrees C.]) After cooling reaction mixture radiationally, toluene 50g and 100g of water were added, liquids were separated, and 100g of water washed the toluene phase further.

[0024] After drying the washed toluene phase with magnesium sulfate, when reduced pressure distilling off of the solvent was carried out, the oil-like reaction mixture was obtained. When the silica gel column chromatography (elution solvent: chloroform) refined this, 1 and 4-screw [bis(4-t-butoxy cull BONIRUMECHIROKISHI -2, 5-dimethylphenyl) methyl] benzene 1.6g (15% of yield) was obtained as a colorless crystal. the decomposition point is 221 degrees C -- 1 H-NMR spectrum and the elemental analysis were as follows.

[0025] delta1.47 (s36H and t-bu-CH3), delta2.07 (s12H and Ph-CH3), delta2.11 (s12H and -Ph-CH3), delta4.50 (s8H and -OCH2 CO), delta5.45 (s2H, Ph3 CH), delta6.45 (s4H, Ph-H), delta6.48 (s4H, Ph-H), delta6.87 (s4H, Ph-H)

Elemental analysis (%)

Analysis value C:73.50, H:7.85, theoretical value C:73.68, H:7.92

[Translation done.]